

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



(11) Publication number: **0 605 196 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **93310442.4**

(51) Int. Cl.⁵: **C23C 4/10, C23C 28/04**

(22) Date of filing: **22.12.93**

(30) Priority: **29.12.92 US 996920**

(43) Date of publication of application:
06.07.94 Bulletin 94/27

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

(71) Applicant: **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, NY 12345 (US)

(72) Inventor: **Beltran, Adrian Maurice**
RD No.2 Peaceable
Ballston Spa, New York 12020 (US)
Inventor: **Shalvoy, Robert Scott**
48 Woodcrest Drive
Scotia, New York 12302 (US)
Inventor: **Lau, Yuk-Chiu**
22 Bluce Spruce Lane
Ballston Lake, New York 12019 (US)

(74) Representative: **Lupton, Frederick**
LONDON PATENT OPERATION,
G.E. TECHNICAL SERVICES Co. INC.,
Essex House,
12/13 Essex Street
London WC2R 3AA (GB)

(54) Thermal barrier coating process.

(57) A process of providing a thermal barrier coating on a metal substrate comprises the steps of:

- a) applying a metallurgical bondcoat (12) to the substrate (10);
- b) depositing a first zirconia layer (14) on the bondcoat (12);
- c) depositing a second zirconia layer (16) on the first zirconia layer (12); and
- d) controlling substrate temperature during steps b) and c) to provide the first zirconia layer (14) with substantially zero porosity and to provide the second zirconia layer (16) with between about 10% and 20% porosity.

A product produced by the process is also disclosed.

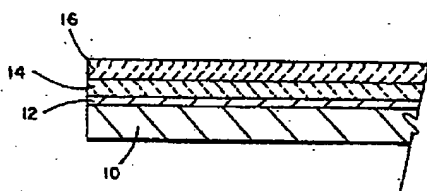


FIG. 1

EP 0 605 196 A1

TECHNICAL FIELD

This invention relates to a process for providing a thermal barrier coating on industrial gas turbine components such as combustion liners and transition pieces.

BACKGROUND PRIOR ART

Thermal barrier coating (TBC) systems are widely used in high temperature applications to provide oxidation and thermal resistance protection to metallic substrates under high thermal gradient conditions. Conventional TBC's are applied by various powder spray deposition processes, and consist of an intermediate metallic bondcoat attached to the substrate and a topcoat of stabilized zirconia. The zirconia may be phase-stabilized with between 6 and 22 weight percent yttria, or alternatively, magnesia, ceria or similar oxides. These coatings typically exhibit an uncracked but porous microstructure. This type of processing is done with minimal substrate preheat, and is limited to a maximum coating thickness of 25 to 30 mil. In addition, thermal cycling resistance is significantly reduced due to coating spallation via cracking and separation between the bondcoat and initial zirconia deposit at that interface.

More recently, superior adherence and thermal cycling resistance of zirconia to a bondcoat has been achieved by virtue of a controlled microstructure. This is obtained by preheating the substrate to at least 600°F. before and during deposition of the zirconia, which produces a dense, columnar deposit which is precracked perpendicular to the interface. This readily allows the deposition and retention of a thick ceramic layer of up to 100 mil in thickness.

Control of the initial zirconia layers deposited via this process is critical to the thermal cycling resistance of this TBC. In part, control is achieved through process parameter optimization and per-pass powder injection rates which are generally lower than conventional processing. Hence, this coating has a higher thermal conductivity per unit thickness than the porous conventional coating described above, by as much as 30 to 50%. Therefore, this coating may have an effective thermal resistance only one-third that of its absolute thickness advantage.

Another process for applying a ceramic thermal barrier to a metallic substrate is disclosed in U.S. Patent No. 4,503,130. This patent describes a process where graded ceramic/metallic layers are applied between the bondcoat and two upper layers of ceramic, one dense and one porous.

In U.S. Patent No. 4,613,259, apparatus is disclosed for controlling powder flow rate in a carrier gas. The apparatus is employed specifically to control the production of graded ceramic/metallic layers on a substrate.

SUMMARY OF THE INVENTION

The objective of this invention is to provide a superior TBC coating through plasma spray deposition of an initial zirconia deposit with a columnar microstructure achieved with controlled substrate preheat. This first or inner layer promotes good adherence, and is followed by a smooth, in-process transition to conditions which favor deposition of a controlled porosity, highly thermal resistive zirconia outer layer.

A more specific objective of this invention is to provide a cost-effective coating process for large surface area components such as industrial landbased gas turbine combustion liners and transition pieces, which typically require TBC coatings over 1500-2000 square inches of surface area.

The advantage of this two-layer zirconia TBC microstructure is that it maximizes thermal cycling resistance and thermal resistivity at an overall lower coating thickness. This will result in reduced manufacturing cycle time and cost. Further reductions in cycle time may be achieved through increases in powder deposition rates, particularly for the outer zirconia layer, since a porous structure may be easier to achieve and control in this manner.

The coating process of this invention thus produces a thermally resistant surface layer comprised of two layers (transitioned through grading of porosity) of stabilized zirconia ceramic attached to an oxidation and corrosion resistant metallic bondcoat, which is itself metallurgically bonded to a metallic substrate.

More specifically, an air plasma spray process used to deposit the inner stabilized-zirconia layer, however, is controlled to produce a dense, columnar microstructure which has lower thermal resistivity, but which is extremely well adhered to the metallic bondcoat and which also provides maximum thermal cycling resistance to the composite, multi-layered coating system. The outer stabilized zirconia layer is applied by the air plasma spray deposition process to produce a controlled microstructure containing minimal cracks and approximately 10 to 20% porosity, which enhances thermal resistivity of the layer.

In accordance with the broader aspects of the invention, therefore, a process is provided for applying a thermal barrier coating to a metallic substrate which comprises the steps of:

- a) applying a metallurgical bondcoat to the substrate;
- b) depositing a first zirconia layer on the bondcoat, the first zirconia layer having a dense, columnar microstructure; and
- c) depositing a second zirconia layer on the first zirconia layer, the second zirconia layer having a microstructure having a porosity of between 10 and 20%.

In another aspect, the invention relates to a gas

turbine component having a thermal barrier coating thereon, applied by the above described process.

By the above described invention, a superior thermal barrier coating is achieved which exhibits excellent adhesion, thermal cycling and oxidation resistance, and high thermal resistivity.

Additional objects and advantages of the invention will become apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a cross section of a metal substrate provided with a thermal barrier coating in accordance with a first exemplary embodiment of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

With reference to the Figure, a schematic illustration of an exemplary embodiment of the invention is shown to include a metallic substrate material 10 with a bondcoat 12 metallurgically bonded thereto. The substrate 10 may be, for example, a large superalloy surface area component of an industrial gas turbine engine. More specifically, the substrate may be a combustion liner or a transition piece (connecting the combustion chamber to the turbine) or other large component which typically requires a thermal barrier coating over 1500-2000 square inches of surface area.

The metallic bondcoat 12 may be applied by a variety of thermal spray processes including air or vacuum plasma, or High Velocity Oxy-Fuel (HVOF) deposition to a suitable thickness, and may comprise MCrAlY chemical compositions, where M is Co, Ni, Fe or combinations of these elements. For example, one such bondcoat may comprise 10-30% weight Chromium, 3-13 wt.% aluminum, and 0.05 to 1.0 wt.% yttrium or other rare earth elements, and the balance M.

An inner stabilized zirconia deposit layer 14 is applied to the bondcoat 12 by an air plasma spray process. The process is controlled (by substrate preheat) to produce a dense (i.e., substantially zero porosity), columnar microstructure which has lower thermal resistivity, but which is extremely well adhered to the metallic bondcoat 12. In this regard, it is not necessary in this process to apply graded layers (transitioning from all metal to all non-metallic) to insure adherence between layer 14 and the metallic bondcoat 12. More specifically, the substrate temperature is initially elevated to a temperature in excess of 600°F. and up to about 1200°F. or higher to provide the dense, columnar microstructure. The thickness of this inner layer 14 is preferably between about 2 and about 20 mil, but may be greater. This inner layer 14 provides maximum thermal cycling resistance to the composite, multi-layered coating system.

Following the deposition of the inner layer 14, the process is continued under conditions which favor the deposition of a controlled porosity, highly thermal resistive zirconia outer layer 16, having a thickness of between about 10 and about 45 mil. The outer zirconia layer 16 is also applied by the air plasma spray deposition process to produce a controlled microstructure containing minimal cracks and approximately a 10 to 20% porosity, which enhances the thermal resistivity of the layer. This is achieved by permitting the substrate to cool to a lower temperature, between ambient and up to about 600°F. As a result of the continuity of the process, a transition zone between the inner and outer layers is created which has a porosity of between 0 and about 10%.

By thus controlling the substrate heat before and during deposit of the zirconia layers 14 and 16, it is possible to control the density/porosity of the layers and thereby maximize the adherence of the inner layer 14 to the bondcoat 12, and at the same time, maximize the thermal resistivity of the outer layer 16.

The advantage of this two-layer zirconia TBC microstructure is that it maximizes thermal cycling resistance and thermal resistivity at a lower total coating thickness. This will result in reduced manufacturing cycle time and cost. Further reductions in cycle time may be achieved through increases in powder deposition rates, particularly for the outer zirconia layer, since a porous structure may be easier to achieve and control in this manner.

While the invention has been described with respect to what is presently regarded as the most practical embodiments thereof, it will be understood by those of ordinary skill in the art that various alterations and modifications may be made which nevertheless remain within the scope of the invention as defined by the claims which follow.

Claims

1. A process of producing a thermal barrier coating on a metal substrate comprising the steps of:
 - a) applying a metallurgical bondcoat to the substrate;
 - b) depositing a first zirconia layer on the bondcoat, the first zirconia layer having a dense, columnar microstructure; and
 - c) depositing a second zirconia layer on the first zirconia layer, the second zirconia layer having a microstructure with a porosity of between 10 and 20%.
2. The process of Claim 1 wherein steps b) and c) are carried out using an air plasma spray process.
3. The process of Claim 1 or 2 wherein step a) is

carried out using a thermal spray process.

4. The process of any preceding claim wherein the substrate is comprised of a superalloy. 5
5. The process of claim 1 wherein the first zirconia layer has a thickness of between about 2 and about 20 mil. 10
6. The process of Claim 1 wherein the second zirconia layer has a thickness of between about 10 and about 45 mil. 15
7. A process of providing a thermal barrier coating on a metal substrate comprising the steps of : 20
 - a) applying a metallurgical bondcoat to the substrate;
 - b) depositing a first zirconia layer on the bondcoat;
 - c) depositing a second zirconia layer on the first zirconia layer; and 25
 - d) controlling substrate temperature during steps b) and c) to provide said first zirconia layer with substantially zero porosity and to provide said second zirconia layer with about 10% porosity.
8. The process of any preceding claim wherein, during step b), the substrate is maintained at a temperature about 600°F. 30
9. The process of any preceding claim wherein during step a), the substrate is maintained at a temperature of less than 600°F. 35
10. The process of any preceding claim wherein said bondcoat comprises an alloy of MCrAlY where M is one of Co, Ni, Fe or combinations thereof. 40
11. A gas turbine component having a surface provided with a thermal barrier coating in accordance with the process of Claim 1. 45

45

50

55

4

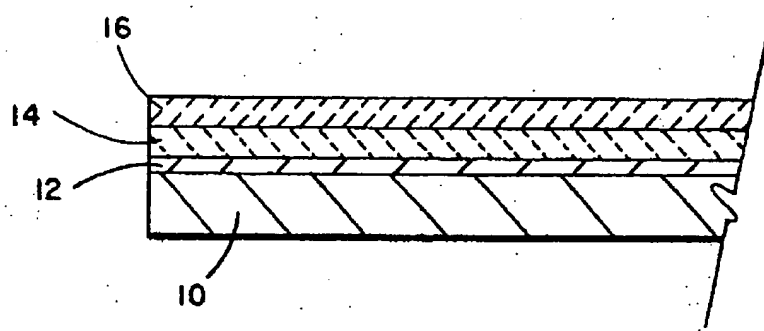


FIG. 1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 93310442.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CLS)
X	EP - A - 0 185 603 (UNITED TECHNOLOGIES)	7,10, 11	C 23 C 4/10 C 23 C 28/04
A	* Fig. 4; fig. 2; abstract *	1-4,6	
X	EP - A - 0 183 638 (UNITED TECHNOLOGIES)	7,10, 11	
A	* Fig. 2; claims 1-11; page 1, lines 1-8 *	1-4,6	
D,X	US - A - 4 613 259 (PACKER ET AL.) * Fig. 5; column 5, lines 20-41; abstract *	7,10, 11	
D,A	US - A - 4 503 130 (BOSSHART ET AL.) * Fig. 2; column 3, lines 19-33; claim 2 *	1-3,6, 7,10, 11	
P,A	WO - A - 93/18 199 (ROLLS-ROYCE PLC) * Abstract; page 11, lines 13-17; fig. 4 *	1,4,5, 6,10, 11	TECHNICAL FIELDS SEARCHED (Int. CLS) C 23 C 4/00 C 23 C 28/00
A	EP - A - 0 366 924 (ALLIED-SIGNAL INC.) * Claims 1,2,9,10; abstract *	1,4, 10,11	
A	WO - A - 92/05 298 (UNITED TECHNOLOGIES) * Claims; page 1, lines 16-19 *	1,4,5, 7,10, 11	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 08-04-1994	Examiner KÖRBER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone V : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

KI'O FORM 1501 01.83 (P0011)